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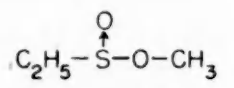
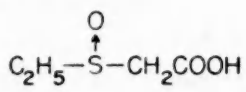
The Preparation of Sulfinic Acids

By T. M. LAAKSO*

Although aromatic sulfinic acids have been known since the early nineteenth century, references to aliphatic sulfinic acids are comparatively few in the literature. In fact, some of the quite simple members are as yet unknown. Some caution must be exercised in interpreting names in the older literature since some sulfones were reported as sulfinic esters and sulfonium compounds as sulfines. The nomenclature of the sulfinic acids is similar to that of the sulfonic acids, i.e., $C_2H_5SO_2H$ is ethanesulfinic acid;

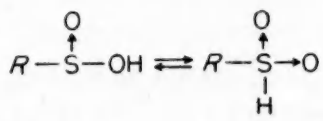


is methyl ethanesulfinate; C_2H_5SOCl is ethanesulfinyl chloride; and

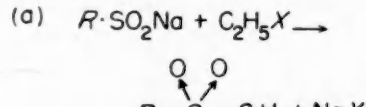


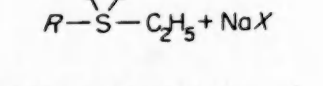
is ethylsulfinylacetic acid.

The exact structure of the sulfinic acids was controversial as late as 1920. Some of their reactions indicated the presence of a hydroxyl group. Others were best explained by assuming the hydrogen was attached directly to the sulfur atom. The formation of derivatives of each has been cited as evidence. When a sodium sulfinate is treated with an alkyl halide, the sulfone (a) is formed;

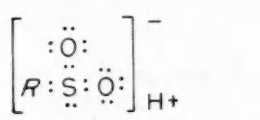


the ester is formed by the action of an alkyl chloro carbonate (b). According to



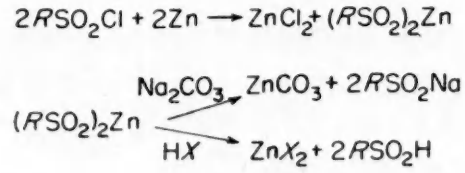


the modern theory of structure, in the sulfinate ion the oxygen and sulfur have



unshared electron pairs, and either may be involved in reactions. The resolution of sulfinic esters by Phillips in 1925 (1) was important in elucidating the structure, as well as being the first evidence of the existence of optical isomers in a neutral compound containing only three groups attached to the central atom.

Sulfinic acids may be prepared by the reduction of sulfonyl chlorides by zinc dust in water (2). This reaction gives zinc sulfinates from which soluble sulfinates or free sulfinic acids may be obtained.



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Good yields of sulfinates are obtained by this method, despite the formation of sulfhydryl compounds by a side reaction. This method is applicable both in the aromatic and aliphatic series, being possible in the latter because of the rather recent availability of aliphatic sulfonyl chlorides. Other reducing agents may be used, sodium sulfite being the most satisfactory.

Another method of preparation of sulfinic acids consists in saturating an acid solution of a diazonium salt with sulfur dioxide, using copper powder as a catalyst (3). This procedure gives very good

$$R\text{N}_2\text{SO}_4\text{H} + 2\text{SO}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{Cu}} R\text{SO}_2\text{H} + \text{N}_2 + 2\text{H}_2\text{SO}_4$$

yields in some cases, depending on the nature of the diazonium compound.

Both aliphatic and aromatic sulfinic acids may be prepared by the reaction of sulfur dioxide with Grignard reagents in ether solution (4). This reaction is analogous to the preparation of fatty acids by carbonation of Grignard reagents.

$$R\,\text{Mg}X + \text{SO}_2 \rightarrow R\text{SO}_2\text{Mg}X \xrightarrow{\text{H}_2\text{O}} R\text{SO}_2\text{H}$$
$$R\text{Mg}X + \text{CO}_2 \rightarrow R\text{CO}_2\text{Mg}X \xrightarrow{\text{H}_2\text{O}} R\text{CO}_2\text{H}$$

The yields of sulfinic acids from this method are not consistently as good as by some other methods; e.g., benzylsulfinic acid is obtained in about 25 percent yield.

Sulfuryl chloride reacts with Grignard reagents to give a sulfinic acid and an alkyl chloride (5).

$$2R\text{MgCl} + \text{SO}_2\text{Cl}_2 \longrightarrow R\text{SO}_2\text{MgCl} + R\text{Cl} + \text{MgCl}_2$$
$$R\text{SO}_2\text{MgCl} + \text{H}_2\text{O} \longrightarrow R\text{SO}_2\text{H} + \text{Mg(OH)Cl}$$

A very good but rather long procedure for the preparation of aliphatic sulfinates is the cleavage of ethylene disulfones by potassium cyanide (6).

$$2R\text{SNa} + \text{BrCH}_2\text{CH}_2\text{Br} \longrightarrow R\text{SCH}_2\text{CH}_2\text{S}R$$
$$R\text{SCH}_2\text{CH}_2\text{S}R + 2\ \text{O}_2 \longrightarrow R\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_2R$$
$$R\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_2R + \text{KCN} \longrightarrow 2R\text{SO}_2\text{K} + \text{CNCH}_2\text{CH}_2\text{CN}$$

Aromatic sulfinic acids are also produced economically in moderate to good yields by what is essentially a Friedel-Crafts type of reaction (7).

$$\text{C}_6\text{H}_6 + \text{SO}_2 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{SO}_2\text{H}$$

Compounds having an olefinic double bond when treated with a mixture of a neutral salt, such as sodium chloride, a Friedel-Crafts catalyst, and an excess of sulfur dioxide also reputedly give good yields of sulfinic acids (8).

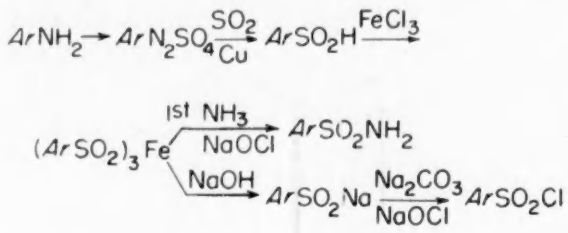
Free aromatic sulfinic acids may usually be obtained by the acidification of aqueous solutions of their salts. The more soluble members may be precipitated quantitatively as the ferric salt from strongly acid solution by the addition of ferric chloride. The ferric salts form orange-colored precipitates which are readily filtered and washed and are quite stable in dry air. This is a characteristic property of sulfinic acids.

Aliphatic sulfinic acids generally are viscous oils which decompose rapidly and are usually isolated as the alkali metal salts. Aromatic sulfinic acids are not quite as unstable, though they will slowly decompose upon long standing. They are readily oxidized, giving sulfonic acids and thiolsulfonic esters.

$$3R\text{SO}_2\text{H} \longrightarrow R\text{SO}_3\text{H} + R\text{SO}_2\text{S}R + \text{H}_2\text{O}$$

This reaction is accelerated by heat and aqueous acids and is used for the preparation of thiolsulfonic acids (9). The sulfinic acids are weaker acids than the corresponding sulfonic acids and have a lower solubility in water. The ferric salts of aromatic sulfinic acids are important intermediates in a series of interesting reactions for the replacement of the

$-NH_2$ group in a compound by the radicals $-SO_2H$, $-SO_3Cl$, and $-SO_2NH_2$ (10).



Among the more important uses of sulfinic acids is the preparation of certain derivatives for use as reducing agents in vat dyeing (i.e., sodium formaldehyde-sulfoxylate). The solubilizing group $-CH_2SO_2Na$ is introduced into many substances, particularly medicinals, by means of sulfinic acids. Certain aryl derivatives are also used in electrodeposition of nickel. Salts of sulfinic acids derived from aliphatic hydrocarbons are used as emulsifying agents in insecticidal sprays.

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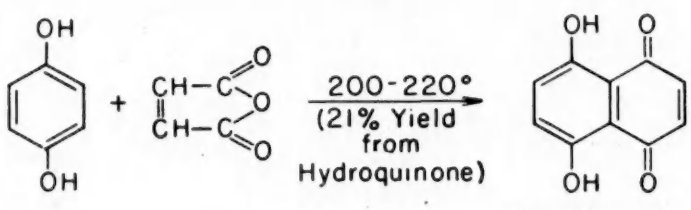
The Reactions of Hydroquinone and Derivatives

By DE WALT S. YOUNG*

(*Conclusion*)

Hydroxyhydroquinone triacetate (1,2, 4-phenenyl triacetate) reacts similarly to form 4-methyl-6,7-dihydroxycoumarin (4-methylesculetin) (92%) (33).

The important dye intermediate quinizarin can be synthesized from hydroquinone by condensation with phthalic anhydride, using sulfuric acid as condensing agent (34). Alternatively, an aluminum chloride–sodium chloride mixture may be used to effect the condensation (35). Similarly, hydroquinone reacts with maleic anhydride in an $AlCl_3$-NaCl melt to form naphthazarin (36).



The procedure has been applied to the synthesis of naphthazarin derivatives from substituted hydroquinones by Kurado and Wada (23).

Hydroquinone undergoes reaction with aliphatic and aromatic amines to produce several derivatives of industrial importance. The commonly used photographic developer, N-methyl-*p*-aminophenol sulfate (Kodak Elon Developing Agent), may be prepared by reaction of hydroquinone with an aqueous solution of methyl amine in an autoclave at 200 C (37) (38). Similarly, compounds used on a large scale as stabilizers for fuels may be made by reaction of hydroquinone with the lower aliphatic amines. In particular, *p*-N-butylaminophenol is a very active oxidation inhibitor for cracked gasoline (39). N-Phenyl *p*-ami-

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nophenol (*p*-anilinophenol) and N,N'-diphenyl-*p*-phenylenediamine may be obtained by condensation of hydroquinone with aniline at 300 C in the presence of alkyl phosphates as catalysts (40) (41).

The monocarboxylic acid of hydroquinone, gentisic acid, has become of great interest in the treatment of rheumatic diseases. It has been suggested as a possible replacement for sodium salicylate, of which it is considered a metabolite (42). A recent patent (43) states that gentisic acid may be prepared in 80% yield (40% conversion) by carboxylation of an aqueous hydroquinone salt in the presence of a sulfide catalyst. Villani and Lang (44) have reported the synthesis of gentisic acid from hydroquinone monomethyl ether (*p*-methoxyphenol) under the conditions of the Reimer-Tiemann reaction with carbon tetrachloride and also from 2,5-dimethoxyacetophenone by alkaline hypochlorite oxidation. A final demethylation step is required in both the latter procedures.

In addition to the preparative procedures described above, most of which employ hydroquinone as starting material, many other hydroquinone derivatives are available through the corresponding quinones by oxidation procedures from substituted amines and phenols (20), and also through the Elbs persulfate oxidation of phenols (45).

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Patent Clause:

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New Eastman Organic Chemicals

T 6823	α,α'-Bi-*p*-toluidine (Techn.) MP 135-139°	100 g.	$1.40
	$NH_2C_6H_4CH_2CH_2C_6H_4NH_2$ . . . MW 212.28	500 g.	5.10
P 5438	*p*-Chloroacetylacetanilide (Pract.) MP 210-212°	10 g.	1.25
	$ClCH_2COC_6H_4NHCOCH_3$ . . . MW 211.65	100 g.	8.00
6834	α-Chloro-N-ethylacetanilide MP 17-18° and 30-32°	10 g.	1.30
	$C_6H_5N(C_2H_5)COCH_2Cl$ . . . MW 197.66	100 g.	8.50
P 6815	(4-Chloro-2-methylphenoxy)acetic Acid (Pract.) (95%)	100 g.	1.25
	$ClC_6H_3(CH_3)OCH_2COOH$ . . . MW 200.62	500 g.	4.15
P 6842	1,2-Cyclohexanedicarboxylic Anhydride (Pract.) MP 33-35°	500 g.	2.05
	$CH(CH_2)_4CHCOOCO$ . . . MW 154.16	1 kg.	3.60